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(56) Documents Cited

WO 97/33198 A1 WO 96/37526 A1
CA Abstract Number 127:227308 & Proc. SPIE-Int. Soc.
Opt. Eng. (1997) 3049 XIV 92-103 CA Abstract Number
127:227269 & J. Photopolym. Sci. Technol. (1997) 10(4)
529-534 CA Abstract Number 66:18889 & Magy. Kem.
Foly. (1966) 72(11) 491-493

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(54) Abstract Title

Bicycloalkene photoresist copolymers

(57) A photoresist includes a copolymer of one or more bicycloalkene derivatives with maleic anhydride and/or vinylene carbonate, and has a molecular weight of 3000 to 100,000. The bicycloalkene derivative is a 5-norbornene- or bicyclo[2.2.2]oct-5-ene-2-carboxylic acid or ester. The photoresist can be used for submicrolithography employing deep ultra violet as a light source. In addition to being of high etch resistance and thermal resistance, the photoresist has good adhesiveness and can be developed in a TMAH solution.

GB 2 320 718

Meanwhile, the resolution of the patterns formed by photolithography is generally proportional to the wavelength of light source. Thus, finer patterns can be formed as the wavelength is shorter. As a result of the effort to find new
 5 light sources suitable to improve the resolution, deep uv (DUV) light was developed for the integration of semiconductor devices into 1 giga or higher scale.

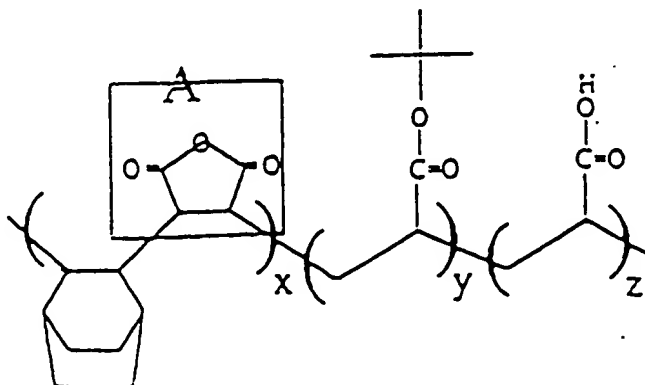
Generally, photoresists are required to be of high etch
 10 resistance and thermal resistance. In addition, the photoresist to be used for ArF should be developed in a 2.38% tetramethylammonium hydroxide (TMAH) solution. However, in fact, it is difficult to obtain a photoresist resin which satisfies those properties entirely.

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For example, the resins having a backbone of poly(methylmethacrylate), which is transparent to the light of the above short wavelengths, are easy to synthesize. But there are problems in practical application owing to their poor etch
 20 resistance and development in TMAH solution. Etch resistance can be improved by introducing aliphatic rings monomers into the main chain. But it is virtually impossible to synthesize the resin having a main chain consisting of aliphatic rings.

25 In order to solve the above problems, AT & T (or Bell Laboratory) developed a resin having a main chain which is substituted for norbornene, acrylate and maleic anhydride, represented by the following formula I:

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In Formula I, the maleic anhydride part A is used with the aim of polymerizing aliphatic cyclo-olefin groups but well dissolved in a 2.38% TMAH solution even in the state of un-exposure. This dissolution can be inhibited by increasing the proportion of the y part, substituted for t-butyl, in the main chain. If so, the z part, functioning to increase the adhesiveness to a substrate, relatively becomes small in proportion, which leads to the release of the photoresist from the substrate, e.g. wafer. As a result, the formation of good patterns is impossible by this method. Bell Laboratory suggested a two-component system including a cholesterol compound as a dissolution inhibitor. This dissolution inhibitor is, however, required to be added in a large quantity, for example, about 30 % by weight of the resin, so that Bell Laboratory's resins are in principle problematic in use for photoresist resin.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to overcome the above problems encountered in prior arts and to provide an ArF photoresist resin which is little dissolved in developing solutions without a chemical change in its structure in addition to being superior in etch resistance, thermal resistance and adhesiveness.

It is an object of the present invention to provide a photoresist copolymer.

It is another object of the present invention to provide a method for preparing the photoresist copolymer.

It is a further object of the present invention to provide a photoresist comprising the photoresist copolymer.

It is still another object of the present invention to provide a method for fabricating the photoresist.

It is still another object of the present invention to provide a method for fabricating an integrated circuit device.

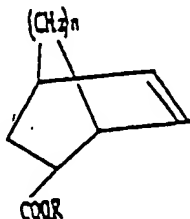
It is still another object of the present invention to provide a partially completely semiconductor device.

DETAILED DESCRIPTION OF THE INVENTION

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The novel photoresist copolymer of the present invention is prepared from one or more bicycloalkene compounds of the following formula II, maleic anhydride of the following formula

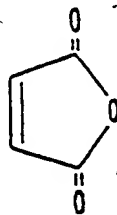
10 [FORMULA II]



15

wherein, R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

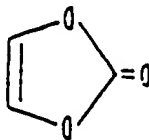
20 [FORMULA III]



25

[FORMULA IV]

30



In Formula II, preferred R group is selected from the group including hydrogen, 2-hydroxyethyl and t-butyl. That is,

35

preferred examples of the bicyclicalkene include 2-hydroxyethyl
5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate,
5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo
[2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-
5 2-carboxylate and / or bicyclo[2,2,2]oct-5-ene-2-carboxylic
acid.

The copolymer of the invention has a molecular weight
ranging from approximately 3,000 to 100,000.

10

One of the preferable copolymers of the invention is
prepared from vinylene carbonate and one or more bicyclic
alkenes wherein R is hydrogen, 2-hydroxy ethyl and t-butyl and
n is 1. That is, it is selected from 2-hydroxyethyl 5-
15 norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-
norbornene 2-carboxylic acid.

The novel copolymers of the present invention, consisting
of one or more the bicycloalkene compound of Formula II, and
20 maleic anhydride of Formula III or vinylene carbonate of Formula
IV, may be prepared according to ordinary radical polymerization
techniques using radical polymerization initiators.

They are polymerized in bulk polymerization or in a
25 solution polymerization. For polymerization solvent,
cyclohexanone, methylethylketone, benzene, toluene, dioxane,
dimethylformamide, tetrahydrofuran alone or the combinations
thereof may be used. Usually, the polymerization is carried out
in the presence of a polymerization initiator, such as
30 benzoylperoxide, 2,2'-azobisisobutyronitrile (AIBN), acetyl
peroxide, lauryl peroxide and t-butylperacetate.

A positive photoresist composition useful for forming
positive fine patterns in semiconductor devices may be obtained
35 by mixing the novel photoresist copolymer of the invention with

a photoacid generator in an organic solvent in a typical manner. Upon formulation, the amount of the copolymer is dependent on the organic solvent, the photoacid generator and the lithography conditions and is preferably about 10-30 % by weight of the organic solvent used.

To fabricating a photoresist, the copolymer of the invention is first dissolved in cyclohexanone or at an amount of 10-30 % by weight and an onium salt or organic sulfonic acid, as a photoacid generator, is added at an amount of about 0.1-10 % by weight of the resist polymer. Then, this solution is filtered with an ultrafine filter to yield a photoresist solution.

This photoresist solution is spin-coated on a silicon wafer and which is, then, soft-baked at a temperature of 80-150 °C for 1-5 min in an oven or on a hot plate. An exposure process is carried out by use of a stepper which employs deep uv light or excimer laser as a light source. Thereafter, the wafer is subjected to post-baking at a temperature of 100-200 °C. An ultrafine positive resist image can be obtained by immersing the post-baked wafer for 90 seconds in a 2.38% TMAH solution.

A better understanding of the present invention may be obtained in light of following examples which are set forth to illustrate, but are not to be construed to limit, the present invention.

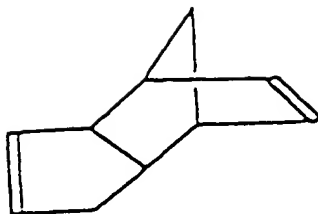
EXAMPLE I

Synthesis of 2-hydroxyethyl 5-norbornene-2-carboxylate

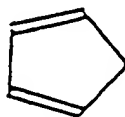
Dicyclopentadiene of the following formula V was cracked at about 120-170 °C, thereby obtaining cyclopentadiene of the following formula VI

[FORMULA V]

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10 [FORMULA VI]

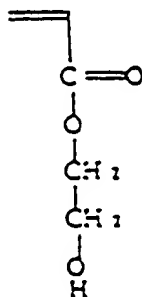


15

Cyclopentadiene of Formula VI and 2-hydroxyethylacrylate of the following formula VII were dissolved at a same rate in ether or tetrahydrofuran. Thereafter, this was reacted at a temperature of about -30 to 60 °C for 24 hours. Thereafter, the solvent was removed by use of a rotary evaporator and the residues were distilled in vacuo to give 2-hydroxyethyl 5-norbornene-2-carboxylate of the following formula VIII which was in an endo- and exo-mixture.

25 [FORMULA VII]

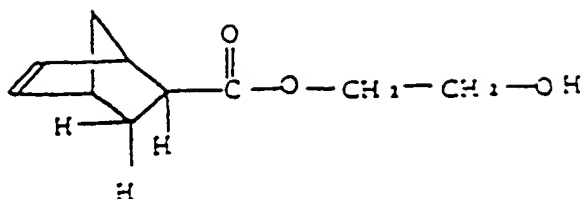
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[FORMULA VIII]

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EXAMPLE II

Synthesis of t-butyl 5-norbornene-2-carboxylate

10

In a reactor, 66 g of cyclopentadiene was first put and then mixed with 500 g of tetrahydrofuran. To the reactor, 128 g of t-butyl acrylate was added. Thereafter, these reactants were subjected to a reaction at a temperature of -30 to 60 °C for 10 hrs with stirring. After the completion of the reaction, the solvent was vaporized in vacuo by use of a rotary evaporator then vacuum distilled to produce the title compound: yield is 90%.

20

EXAMPLE III

Synthesis of Copolymer

91 g of the 2-hydroxyethyl 5-norbornene-2-carboxylate synthesized in Example I, 97 g of the t-butyl 5-norbornene-2-carboxylate synthesized in Example II, and 86 g of vinylene carbonate were put in a reactor and which was, then, purged with a nitrogen atmosphere. A reaction was performed for 6 hrs at 65-120 °C under a pressure of 50-200 atm. After the completion of the reaction, a part of the solvent was removed by a rotary evaporator and residue of the solvent was precipitated in ethyl ether. The precipitate was filtered and dried in a vacuum oven. The resulting product was used as a photoresist resin.

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EXAMPLE IV

Synthesis of Copolymer

91 g of the 2-hydroxyethyl 5-norbornene-2-carboxylate synthesized in Example I, 97 g of the t-butyl 5-norbornene-2-carboxylate synthesized in Example II, and 98 g of maleic anhydride were put into a reactor and which was, then, purged
5 with a nitrogen atmosphere. A reaction was performed for 6 hrs at 65-120 °C under a pressure of 50-200 atm. After the completion of the reaction, a part of the solvent was removed by a rotary evaporator and residue of the solvent was precipitated in ethyl ether. The precipitate was filtered and dried in a
10 vacuum oven. The resulting product was used as a photoresist resin.

EXAMPLE V

Synthesis of Copolymer

15

98 g of bicyclo [2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of bicyclo [2,2,2] oct-5-ene-t-butylacrylate and 86 g of vinylene carbonate were put into a reactor and then, mixed with 2 L of tetrahydrofuran solvent. Thereafter, 1.5 g of
20 azobisisobutyronitrile (AIBN) was put into the reactor and then, the reactor was purged with a nitrogen atmosphere. A reaction was performed for 6 hrs at 65 °C. After the completion of the reaction, a part of the solvent was removed by a rotary evaporator and residue of the solvent was precipitated in ethyl
25 ether. The precipitate was filtered and dried in a vacuum oven. The resulting product was used as a photoresist resin.

EXAMPLE VI

Synthesis of Copolymer

30

98 g of bicyclo [2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of bicyclo [2,2,2] oct-5-ene-t-butylacrylate and 86 g of maleic anhydride were put into a reactor and then, mixed with 2 L of tetrahydrofuran solvent. Thereafter, 1.5 g of
35 azobisisobutyronitrile (AIBN) was put into the reactor and then,

the reactor was purged with a nitrogen atmosphere. A reaction was performed for 6 hrs at 65 °C. After the completion of the reaction, a part of the solvent was removed by a rotary evaporator and residue of the solvent was precipitated in ethyl ether. The precipitate was filtered and dried in a vacuum oven. The resulting product was used as a photoresist resin.

EXAMPLE VII

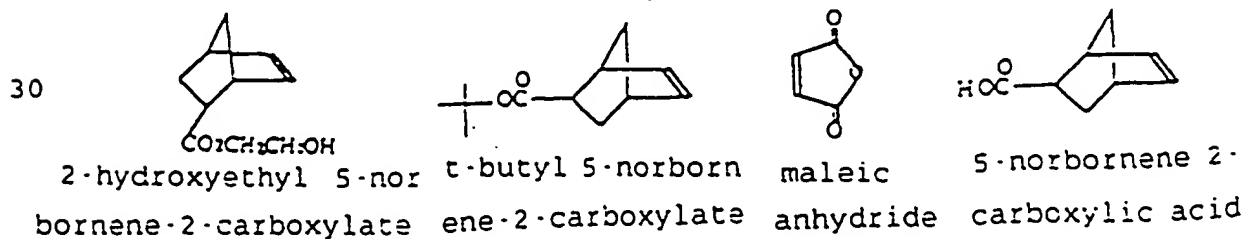
Synthesis of ArF Photoresist Resin

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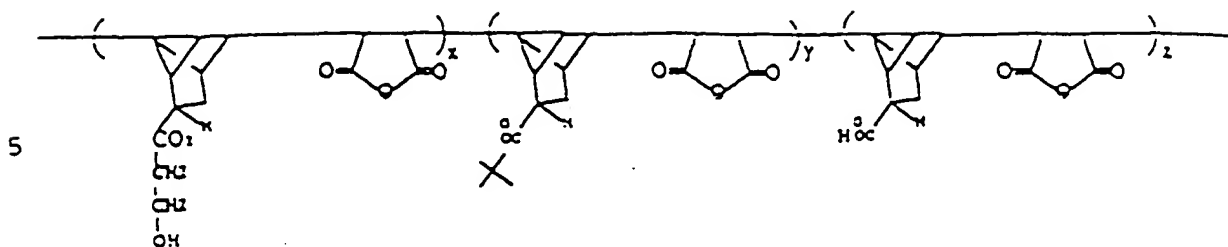
Synthesis of poly[2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene 2-carboxylic acid / maleic anhydride].

1 mole of maleic anhydride of the following formula IX, 0.05-0.8 moles of 2-hydroxyethyl 5-norbornene-2-carboxylate, 0.5-0.95 moles of t-butyl 5-norbornene-2-carboxylate and 0.01 to 0.2 moles of 5-norbornene 2-carboxylic acid were dissolved in tetrahydrofuran or toluene. Thereafter, it was dissolved in a solvent. A radical reaction was executed at a temperature of about 60-70 °C for 4-24 hours under a nitrogen or argon atmosphere in the presence of 0.5-10 g of azobisisobutyronitrile (AIBN), as an initiator. The resin thus produced by this polymerization was precipitated in ethyl ether or hexane and dried to yield poly[2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene 2-carboxylic acid / maleic anhydride] resin of the following formula X.

[FORMULA IX]



[FORMULA X]



EXAMPLE VIII

10 Preparation of Photoresist Film and Formation of Pattern

10 g of poly[2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene 2-carboxylic acid / maleic anhydride] were dissolved in 40 g of 3-methoxymethyl propionate solvent and added with about 0.02-1 g of triphenyl sulfonium triflate or dibutylnaphthyl sulfonium triflate or mixture of these two photoacid generator. After being well stirred, the mixture passed through a 0.10 μm filter. This filtrate was coated on a wafer and patterned. When the 20 coat was about 0.6 μm thick, a vertical L/S pattern was obtained with a resolution of 0.14 μm .

As described hereinbefore, the photoresist prepared from the novel copolymer of the invention is superior in etch 25 resistance and thermal resistance. In addition, it can be developed in a 2.38 % TMAH solution. It also shows such good adhesiveness that 0.15 μm L/S patterns with satisfactory resolution and depth of focus can be obtained from the photoresist coat 0.7 μm thick. Consequently, the introduction 30 of, for example, 2-hydroxyethyl 5-norbornene-2-carboxylate into the backbone of a resin allows for a synthesis of photoresist excellent in adhesiveness.

The present invention has been described in an illustrative 35 manner, and it is to be understood the terminology used is

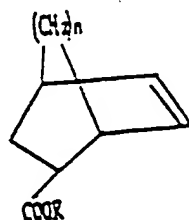
intended to be in the nature of description rather than of limitation.

Many modifications and variations of the present invention
5 are possible in light of the above teachings. Therefore, it is
to be understood that within the scope of the appended claims,
the invention may be practiced otherwise than as specifically
described.

WHAT IS CLAIMED IS:

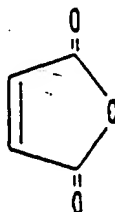
1. A photorésist copolymer which being polymerized from one or more compounds selected from one or more bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV:
[FORMULA II]

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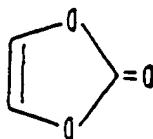


- 15 wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,
[FORMULA III]

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- 25 [FORMULA IV]



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2. A photoresist copolymer in accordance with claim 1, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo (2,2,2)oct-5-ene-2-carboxylate, t-butyl
- 35

bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

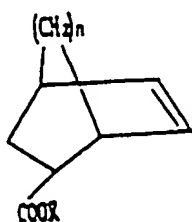
3. A photoresist copolymer in accordance with claim 1, wherein
5 said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

4. A photoresist copolymer in accordance with claim 1, wherein
said copolymer ranges, in molecular weight, from about 3,000 to
10 100,000.

5. A photoresist copolymer in accordance with claim 1, wherein
said copolymer is prepared by copolymerizing vinylene carbonate
and one or more bicycloalkenes wherein R is hydrogen, 2-
15 hydroxyethyl or t-butyl and n is 1.

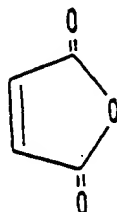
6. A photoresist copolymer in accordance with claim 5, wherein
said bicycloalkenes are selected from the group including 2-
hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-
20 carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl
bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl
bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-
ene-2-carboxylic acid.

25 7. A method for preparing a photoresist copolymer which
comprises the step of: copolymerizing from one or more compounds
selected from the group including one or more bicycloalkenes of
the following formula II, a maleic anhydride of the following
formula III or a vinylene carbonate of the following formula IV:
30 [FORMULA II]

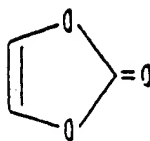


wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

[FORMULA III]



[FORMULA IV]



8. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

9. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

10. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said copolymer ranges, in molecular weight, from about 3,000 to 100,000.

11. A method for preparing a photoresist copolymer in accordance with claim 7, said one or more compounds selected

from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized using radical polymerization initiators.

5

12. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said copolymer is prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

10

13. A method for preparing a photoresist copolymer in accordance with claims 12, wherein said vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 are copolymerized using radical
15 polymerization initiators.

14. A method for preparing a photoresist copolymer in accordance with any one of claims 11 and 13, wherein said radical polymerization initiators are selected from the group
20 including benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

15. A method for preparing a photoresist copolymer in accordance with claim 7, said one or more compounds selected
25 from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized by using bulk polymerization or a solution polymerization.

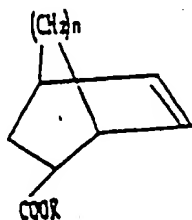
30 16. A method for preparing a photoresist copolymer in accordance with claim 15, wherein said polymerization solvent is selected from the group including cyclohexanone, methylethylketone, benzene, toluene, dioxane, dimethylformamide, tetrahydrofuran alone or the combinations thereof.

35

17. A photoresist, which comprises a copolymer being copolymerized from one or more compounds selected from the group including one or more bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV:

[FORMULA II]

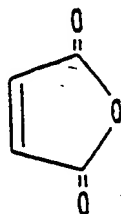
10



15 wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

[FORMULA III]

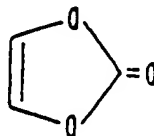
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[FORMULA IV]

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18. A photoresist in accordance with claim 17, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-

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carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and / or bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

5

19. A photoresist in accordance with claim 17, wherein said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

10 20. A photoresist in accordance with claim 17, wherein said copolymer ranges, in molecular weight, from about 3,000 to 100,000.

21. A photoresist in accordance with claim 17, wherein said
15 copolymer is prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

22. A photoresist in accordance with claim 21, wherein said
20 bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-
25 ene-2-carboxylic acid.

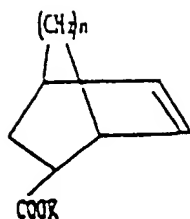
23. A method for preparing a photoresist which comprises the steps of: providing a copolymer being copolymerized from one or more compounds selected from the group including one or more
30 bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV;

mixing said copolymer and a sensitizer in an organic solvent, to produce a photoresist solution.

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[FORMULA II]

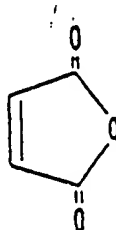
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wherein R represents hydrogen or a straight or branched alkyl
 10 containing 1-10 substituted or non-substituted carbon atoms; and
 n is 1 or 2,

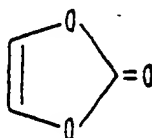
[FORMULA III]

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[FORMULA IV]

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24. A method for preparing a photoresist in accordance with
 claim 23, wherein said bicycloalkenes are selected from the
 group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-
 butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic
 30 acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-
 butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and
 bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

25. A method for preparing a photoresist in accordance with
 35 claim 23, wherein said R is selected from the group including

hydrogen, 2-hydroxyethyl, and t-butyl.

26. A method for preparing a photoresist in accordance with claim 23, wherein said copolymer ranges, in molecular weight,
5 from about 3,000 to 100,000.

27. A method for preparing a photoresist in accordance with claim 23, said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic
10 anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized using radical polymerization initiators.

28. A method for preparing a photoresist in accordance with claim 23, wherein said copolymer is prepared by copolymerizing
15 vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

29. A method for preparing a photoresist in accordance with claims 28, wherein said vinylene carbonate and one or more
20 bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 are copolymerized using radical polymerization initiators.

30. A method for preparing a photoresist in accordance with any one of claims 27 and 29, wherein said radical polymerization
25 initiators are selected from the group including benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

30

31. A method for preparing a photoresist in accordance with claim 23, said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic
anhydride of the formula III or a vinylene carbonate of the
35 formula IV are copolymerized by using bulk polymerization or a

solution polymerization method.

32. A method for preparing a photoresist in accordance with claim 23, wherein said organic solvent is selected from the group including cyclohexanone, methylethylketone, benzene, toluene, dioxane, dimethylformamide, tetrahydrofuran alone or the combinations thereof.

33. A method for preparing a photoresist in accordance with claim 23, wherein said sensitizer comprises a photoacid generator which is selected from the group including an onium salt or organic sulfonic acid.

34. A method for preparing a photoresist which comprises the following steps (i) to (iii):

(i) step of dissolving 9 to 11 g of poly (2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylate / maleic anhydride) copolymer resin in 39 to 42 g of methyl 3-methoxypropionate solvent;

(ii) step of adding 0.02 to 1 g of triphenyl sulfonium triflate or dibuthynaphthyl sulfonium triflate or mixture of these two photoacid generators in the reaction product of the step (i); and

(iii) step of stirring and filtering the reaction product of the step (ii) to produce a photoresist.

35. A method for synthesizing a monomer which comprising steps of: putting a cyclopentadiene in a reactor and mixing with a tetrahydrofuran solvent;

adding a t-butyl acrylate to the reactor;

stirring with said reactants and then reacting on said reactants;

removing said solvent by a rotary evaporator after the completion of the reaction; and

reducing a pressure and distilling after removing said

solvent, to produce a t-butyl 5-norbornene-2-carboxylate.

36. A method for synthesizing a monomer in accordance with claim 35, wherein said method uses about 66 g the
5 cyclopentadiene, about 500 g of the tetrahydrofuran solvent and about 128 g of the t-butyl acrylate.

37. A method for synthesizing a monomer in accordance with claim 35, said stirring step is carried out for 9 to 11 hours at
10 the temperature of about -20 to 70 °C.

38. A method for synthesizing a monomer in accordance with claim 35, said stirring step is carried out for 10 hours at the temperature of about -30 to 60 °C.

15

39. A method for synthesizing a monomer which comprises the following steps (i) to (iv):

(i) dissolving a cyclopentadiene of the following formula VI and 2-hydroxyethylacrylate of the following formula VII at the
20 same rate in ether or tetrahydrofuran solvent;

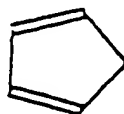
(ii) reacting at a temperature of about -30 to 60 °C for 24 hours the reaction product of the step (i);

(iii) removing the solvent by a rotary evaporator after the completion of the reaction;

25 (iv) reducing a pressure and distilling the reaction product of the step (iii), to produce a 2-hydroxyethyl 5-norbornene-2-carboxylate.

[Formula VI]

30



35

[Formula VII]



40. A method for synthesizing a monomer in accordance with claim 39, wherein said cyclopentadiene is obtained by cracking a dicyclopentadiene of the following formula V at a temperature of about 120 to 170 °C.

[Formula V]



41. A process for preparing a photoresist copolymer which comprises the following steps (i) to (vi):

(i) step of putting a 2-hydroxyethyl 5-norbornene-2-carboxylate, a t-butyl 5-norbornene-2-carboxylate and a vinylene carbonate into a reactor;

(ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);

(iii) step of reacting for the reaction product of the step (ii) for 5 to 7 hours at 50 to 140 °C under the pressure of 30 to 230 atm;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

5

42. A process for preparing a photoresist copolymer in accordance with claim 41, wherein said process which comprises the following steps (i) to (vi):

(i) step of putting 91 g of a 2-hydroxydthyl 5-norbornene-
10 2-carboxylate, 97 g of a t-butyl 5-norbornene-2-carboxylate and 86 g of vinylene carbonate into a reactor;

(ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);

(iii) step of reacting for the reaction product of the step
15 (ii) for 6 hours at 65 to 120 °C under the pressure of 50 to 200 atm;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a
20 ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

43. A process for preparing a photoresist copolymer which
25 comprises the following steps (i) to (vi):

(i) step of putting a 2-hydroxydthyl 5-norbornene-2-carboxylate, a t-butyl 5-norbornene-2-carboxylate and a maleic anhydride into a reactor;

(ii) step of purging with a nitrogen atmosphere the
30 reaction product of the step (i);

(iii) step of reacting for the reaction product of the step (ii) for 5 to 7 hours at 50 to 140 °C under the pressure of 30 to 230 atm;

(iv) step of removing a part of the solvent by a rotary
35 evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

5

44. A process for preparing a photoresist copolymer in accordance with claim 43, wherein said process which comprises the following steps (i) to (vi):

(i) step of putting 91 g of a 2-hydroxyethyl 5-norbornene-
10 2-carboxylate, 97 g of a t-butyl 5-norbornene-2-carboxylate and 98 g of maleic anhydride into a reactor;

(ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);

(iii) step of reacting for the reaction product of the step
15 (ii) for 6 hours at 65 to 120 °C under the pressure of 50 to 200 atm;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a
20 ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

45. A process for preparing a photoresist copolymer which
25 comprises the following steps (i) to (vii):

(i) step of putting a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and a vinylene carbonate into a reactor;

(ii) step of adding a tetrahydrofuran solvent into the
30 reaction product of the step (i);

(iii) step of adding an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step
35 (iii) for 5 to 8 hours at a temperature of 50 to 80 °C;

(v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

5 (vii) step of filtering and drying the precipitate of the step (vi) to produce a photoresist copolymer.

46. A process for preparing a photoresist copolymer in accordance with claim 45, wherein said process which comprises
10 the following steps (i) to (vii):

(i) step of putting 98 g of a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and 86 g of a vinylene carbonate into a reactor;

(ii) step of adding 2 L of a tetrahydrofuran solvent into
15 the reaction product of the step (i);

(iii) step of adding 1.5 g of an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step
20 (iii) for 6 hours at 65 °C;

(v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

25 (vii) step of filtering and drying the precipitate of the step (vi) to produce a photoresist copolymer.

47. A process for preparing a photoresist copolymer which comprises the following steps (i) to (vii):

30 (i) step of putting a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and a maleic anhydride into a reactor;

(ii) step of adding a tetrahydrofuran solvent into the reaction product of the step (i);

35 (iii) step of adding an azobisisobutyronitrile (AIBN) into

the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step (iii) for 5 to 8 hours at a temperature of 50 to 80 °C;

5 (v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

(vii) step of filtering and drying the precipitate of the
10 step (vi) to produce a photoresist copolymer.

48. A process for preparing a photoresist copolymer in accordance with claim 47, wherein said process which comprises the following steps (i) to (vii):

15 (i) step of putting 98 g of a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and 98 g of a maleic anhydride into a reactor;

(ii) step of adding 2 L of a tetrahydrofuran solvent into the reaction product of the step (i);

20 (iii) step of adding 1.5 g of an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step

(iii) for 6 hours at 65 °C;

25 (v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

(vii) step of filtering and drying the precipitate of the
30 step (vi) to produce a photoresist copolymer.

49. A process for preparing a photoresist copolymer which comprises the following steps (i) to (iv):

(i) step of dissolving 1 mole of maleic anhydride of the
35 following formula IX, 0.05 to 0.8 moles of a 2-hydroxyethyl 5-

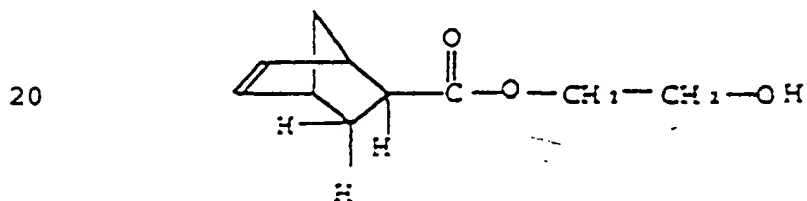
norbornene-2-carboxylate, 0.5 to 0.95 moles of t-butyl 5-norbornene-2-carboxylate and 0.01 to 0.2 moles of 5-norbornene-2-carboxylic acid in tetrahydrofuran or toluene solvent;

(ii) step of putting 0.5 to 1.0 g of an azobisisobutyronitrile (AIBN) initiator in the reaction product of the step (i);

(iii) step of reacting the reaction product of the step (ii) for 4 to 24 hours at 65 to 70 °C under a nitrogen or argon atmosphere; and

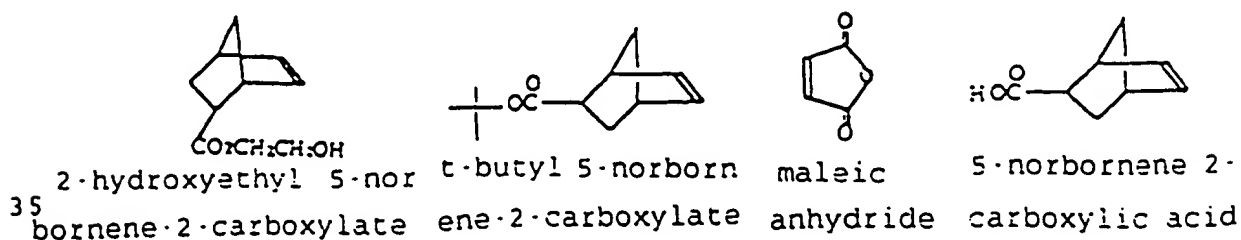
(iv) step of precipitating and drying the reaction product of the step (iii) to produce poly (2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylate / maleic anhydride) photoresist copolymer.

50. A photoresist copolymer which comprises a monomer of 2-hydroxyethyl 5-norbornene-2-carboxylate of the following formula VIII:

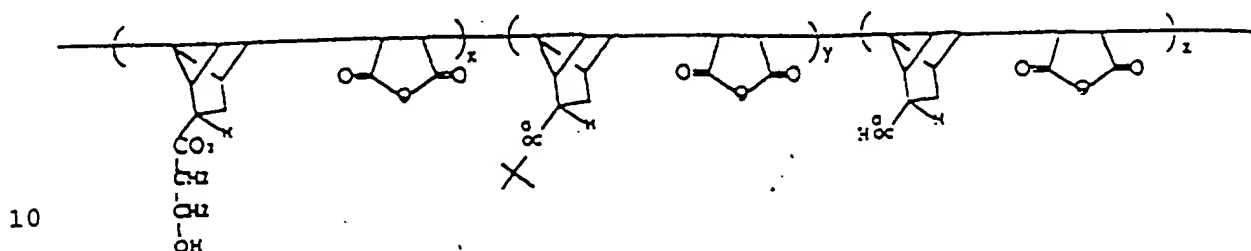


51. A photoresist copolymer in accordance with claim 50, wherein said monomer is synthesized from cyclopentadiene and 2-hydroxyethyl acrylate.

52. A photoresist copolymer in accordance with claim 50, wherein said monomer is prepared by polymerizing said repeating unit with the monomer of the following formula IX:



53. A photoresist copolymer in accordance with claim 50, wherein said resin comprising poly(2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene 2-carboxylic acid / maleic anhydride) of the following formula X:



54. A method of fabricating an integrated circuit device, said method comprising steps of:

15 providing a substrate;

applying a film of resist comprising a photoresist copolymer being polymerized from one or more compounds selected from one or more bicycloalkenes of the following formula II, maleic anhydride of the following formula III or vinylene

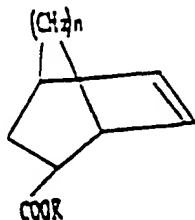
20 carbonate the following formula IV;

exposing a portion of the film of resist using electromagnetic radiation; and

developing said film of resist to form an exposed portion of said substrate corresponding to said portion of said exposed film and performing a process of semiconductor manufacturing on said exposed portion of said substrate.

[FORMULA II]

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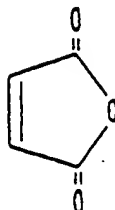


35 wherein R represents hydrogen or a straight or branched alkyl

containing 1-10 substituted or non-substituted carbon atoms; and
n is 1 or 2,

[FORMULA III]

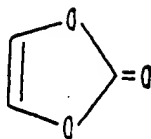
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[FORMULA IV]

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20 55. A method of fabricating an integrated circuit device in
accordance with claim 54, wherein said bicycloalkenes are
selected from the group including 2-hydroxyethyl 5-norbornene-2-
carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-
carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-
25 carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and
bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

56. A method of fabricating an integrated circuit device in
accordance with claim 54, wherein said R is selected from the
30 group including hydrogen, 2-hydroxyethyl, and t-butyl.

57. A method of fabricating an integrated circuit device in
accordance with claim 54, wherein said copolymer ranges, in
molecular weight, from about 3,000 to 100,000.

35

58. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized using
5 radical polymerization initiators.

59. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said photoresist copolymer is
10 prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 using radical polymerization initiators.

60. A method of fabricating an integrated circuit device in accordance with any one of claim 58 and 59, wherein said radical polymerization initiators are selected from the group including
15 benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

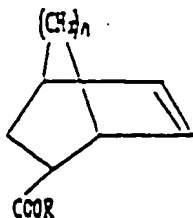
20 61. A partially completely semiconductor device, said device comprising:

a substrate; and

a film of resist comprising a photoresist copolymer being polymerized from one or more compounds selected from one or more
25 bicycloalkenes of the following formula II, maleic anhydride of the following formula III or vinylene carbonate the following formula IV overlying said substrate.

[FORMULA II]

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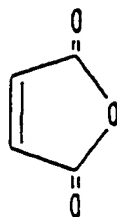


35 wherein R represents hydrogen or a straight or branched alkyl

containing 1-10 substituted or non-substituted carbon atoms; and
n is 1 or 2,

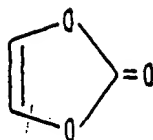
[FORMULA III]

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[FORMULA IV]

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15 62. A partially completely semiconductor device in accordance
with claim 61, wherein said bicycloalkenes are selected from the
group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-
butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic
acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-
20 butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and
bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

63. A partially completely semiconductor device in accordance
with claim 61, wherein said R is selected from the group
25 including hydrogen, 2-hydroxyethyl, and t-butyl.

64. A partially completely semiconductor device in accordance
with claim 61, wherein said copolymer ranges, in molecular
weight, from about 3,000 to 100,000.

30

65. A partially completely semiconductor device in accordance
with claim 61, wherein said photoresist copolymer is prepared by
copolymerizing vinylene carbonate and one or more bicycloalkenes
wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

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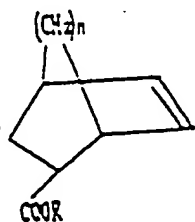
66. A partially completely semiconductor device in accordance with claim 65, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

Amendments to the claims have been filed as follows

WHAT IS CLAIMED IS:

1. A photoresist copolymer which being polymerized from one or more compounds selected from one or more bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV:
[FORMULA II]

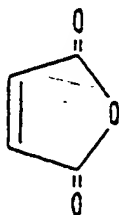
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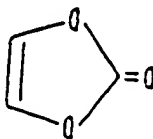
- 15 wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

[FORMULA III]

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25 [FORMULA IV]



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2. A photoresist copolymer in accordance with claim 1, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl

bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

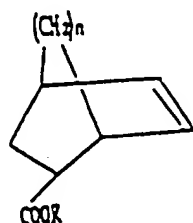
3. A photoresist copolymer in accordance with claim 1, wherein
5 said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

4. A photoresist copolymer in accordance with claim 1, wherein
said copolymer ranges, in molecular weight, from about 3,000 to
10 100,000.

5. A photoresist copolymer in accordance with claim 1, wherein
said copolymer is prepared by copolymerizing vinylene carbonate
and one or more bicycloalkenes wherein R is hydrogen, 2-
15 hydroxyethyl or t-butyl and n is 1.

6. A photoresist copolymer in accordance with claim 5, wherein
said bicycloalkenes are selected from the group including 2-
hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-
20 carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl
bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl
bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-
ene-2-carboxylic acid.

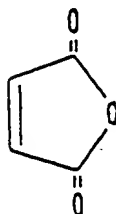
25 7. A method for preparing a photoresist copolymer which
comprises the step of: copolymerizing from one or more compounds
selected from the group including one or more bicycloalkenes of
the following formula II, a maleic anhydride of the following
formula III or a vinylene carbonate of the following formula IV:
30 [FORMULA II]



wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

[FORMULA III]

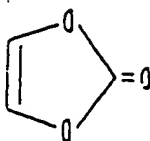
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[FORMULA IV]

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8. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

25

9. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

30 10. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said copolymer ranges, in molecular weight, from about 3,000 to 100,000.

11. A method for preparing a photoresist copolymer in accordance with claim 7, said one or more compounds selected

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from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized using radical polymerization initiators.

5

12. A method for preparing a photoresist copolymer in accordance with claim 7, wherein said copolymer is prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

10

13. A method for preparing a photoresist copolymer in accordance with claims 12, wherein said vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 are copolymerized using radical
15 polymerization initiators.

14. A method for preparing a photoresist copolymer in accordance with any one of claims 11 and 13, wherein said radical polymerization initiators are selected from the group
20 including benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

15. A method for preparing a photoresist copolymer in accordance with claim 7, said one or more compounds selected
25 from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized by using bulk polymerization or a solution polymerization.

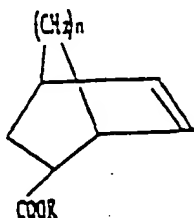
30 16. A method for preparing a photoresist copolymer in accordance with claim 15, wherein said polymerization solvent is selected from the group including cyclohexanone, methylethylketone, benzene, toluene, dioxane, dimethylformamide, tetrahydrofuran alone or the combinations thereof.

35

17. A photoresist, which comprises a copolymer being copolymerized from one or more compounds selected from the group including one or more bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV:

[FORMULA II]

10



15 wherein R represents hydrogen or a straight or branched alkyl containing 1-10 substituted or non-substituted carbon atoms; and n is 1 or 2,

[FORMULA III]

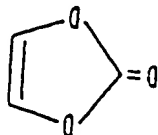
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[FORMULA IV]

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18. A photoresist in accordance with claim 17, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-

carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and / or bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

5

19. A photoresist in accordance with claim 17, wherein said R is selected from the group including hydrogen, 2-hydroxyethyl, and t-butyl.

10 20. A photoresist in accordance with claim 17, wherein said copolymer ranges, in molecular weight, from about 3,000 to 100,000.

21. A photoresist in accordance with claim 17, wherein said
15 copolymer is prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

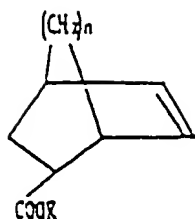
22. A photoresist in accordance with claim 21, wherein said
20 bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-
25 ene-2-carboxylic acid.

23. A method for preparing a photoresist which comprises the steps of: providing a copolymer being copolymerized from one or more compounds selected from the group including one or more
30 bicycloalkenes of the following formula II, a maleic anhydride of the following formula III or a vinylene carbonate of the following formula IV;

mixing said copolymer and a sensitizer in an organic solvent, to produce a photoresist solution.

[FORMULA II]

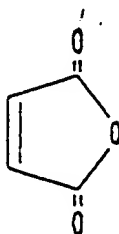
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wherein R represents hydrogen or a straight or branched alkyl
 10 containing 1-10 substituted or non-substituted carbon atoms; and
 n is 1 or 2,

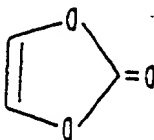
[FORMULA III]

15



[FORMULA IV]

20



25

24. A method for preparing a photoresist in accordance with
 claim 23, wherein said bicycloalkenes are selected from the
 group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-
 butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic
 30 acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-
 butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and
 bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

25. A method for preparing a photoresist in accordance with
 35 claim 23, wherein said R is selected from the group including

hydrogen, 2-hydroxyethyl, and t-butyl.

26. A method for preparing a photoresist in accordance with claim 23, wherein said copolymer ranges, in molecular weight,
5 from about 3,000 to 100,000.

27. A method for preparing a photoresist in accordance with claim 23, said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic
10 anhydride of the formula III or a vinylene carbonate of the formula IV are copolymerized using radical polymerization initiators.

28. A method for preparing a photoresist in accordance with
15 claim 23, wherein said copolymer is prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

29. A method for preparing a photoresist in accordance with
20 claims 28, wherein said vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 are copolymerized using radical polymerization initiators.

25 30. A method for preparing a photoresist in accordance with any one of claims 27 and 29, wherein said radical polymerization initiators are selected from the group including benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

30

31. A method for preparing a photoresist in accordance with claim 23, said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic
anhydride of the formula III or a vinylene carbonate of the
35 formula IV are copolymerized by using bulk polymerization or a

solution polymerization method.

32. A method for preparing a photoresist in accordance with claim 23, wherein said organic solvent is selected from the group including cyclohexanone, methylethylketone, benzene, 5 toluene, dioxane, dimethylformamide, tetrahydrofuran alone or the combinations thereof.

33. A method for preparing a photoresist in accordance with claim 23, wherein said sensitizer comprises a photoacid generator which is selected from the group including an onium salt or organic sulfonic acid.

34. A method for preparing a photoresist which comprises the following steps (i) to (iii):

(i) step of dissolving 9 to 11 g of poly (2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylate / maleic anhydride) copolymer resin in 39 to 42 g of methyl 3-methoxypropionate solvent;

20 (ii) step of adding 0.02 to 1 g of triphenyl sulfonium triflate or dibuthynaphthyl sulfonium triflate or mixture of these two photoacid generators in the reaction product of the step (i); and

(iii) step of stirring and filtering the reaction product 25 of the step (ii) to produce a photoresist.

35. A method for synthesizing a monomer which comprising steps of: putting a cyclopentadiene in a reactor and mixing with a tetrahydrofuran solvent;

30 adding a t-butyl acrylate to the reactor;

stirring with said reactants and then reacting on said reactants;

removing said solvent by a rotary evaporator after the completion of the reaction; and

35 reducing a pressure and distilling after removing said

solvent, to produce a t-butyl 5-norbornene-2-carboxylate.

36. A method for synthesizing a monomer in accordance with claim 35, wherein said method uses about 66 g the cyclopentadiene, about 500 g of the tetrahydrofuran solvent and about 128 g of the t-butyl acrylate.

37. A method for synthesizing a monomer in accordance with claim 35, said stirring step is carried out for 9 to 11 hours at the temperature of about -20 to 70 °C.

38. A method for synthesizing a monomer in accordance with claim 35, said stirring step is carried out for 10 hours at the temperature of about -30 to 60 °C.

15

39. A method for synthesizing a monomer which comprises the following steps (i) to (iv):

(i) dissolving a cyclopentadiene of the following formula VI and 2-hydroxyethylacrylate of the following formula VII at the same rate in ether or tetrahydrofuran solvent;

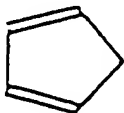
(ii) reacting at a temperature of about -30 to 60 °C for 24 hours the reaction product of the step (i);

(iii) removing the solvent by a rotary evaporator after the completion of the reaction;

(iv) reducing a pressure and distilling the reaction product of the step (iii), to produce a 2-hydroxyethyl 5-norbornen-2-carboxylate.

[Formula VI]

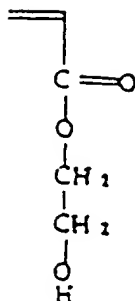
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[Formula VIII]

5

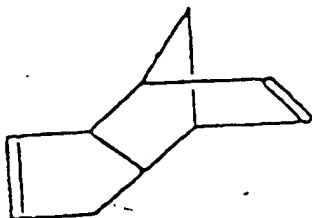


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40. A method for synthesizing a monomer in accordance with claim 39, wherein said cyclopentadiene is obtained by cracking a dicyclopentadiene of the following formula V at a temperature of about 120 to 170 °C.

[Formula V]

20



41. A process for preparing a photoresist copolymer which comprises the following steps (i) to (vi):

- (i) step of putting a 2-hydroxyethyl 5-norbornene-2-carboxylate, a t-butyl 5-norbornene-2-carboxylate and a vinylene carbonate into a reactor;
- (ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);
- (iii) step of reacting for the reaction product of the step (ii) for 5 to 7 hours at 50 to 140 °C;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

5

42. A process for preparing a photoresist copolymer in accordance with claim 41, wherein said process which comprises the following steps (i) to (vi):

(i) step of putting 91 g of a 2-hydroxydthyl 5-norbornene-10 2-carboxylate, 97 g of a t-butyl 5-norbornene-2-carboxylate and 86 g of vinylene carbonate into a reactor;

(ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);

(iii) step of reacting for the reaction product of the step 15 (ii) for 6 hours at 65 to 120 °C under the pressure of 50 to 200 atm;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a 20 ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

43. A process for preparing a photoresist copolymer which 25 comprises the following steps (i) to (vi):

(i) step of putting a 2-hydroxydthyl 5-norbornene-2-carboxylate, a t-butyl 5-norbornene-2-carboxylate and a maleic anhydride into a reactor;

(ii) step of purging with a nitrogen atmosphere the 30 reaction product of the step (i);

(iii) step of reacting for the reaction product of the step (ii) for 5 to 7 hours at 50 to 140 °C;

(iv) step of removing a part of the solvent by a rotary 35 evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

5

44. A process for preparing a photoresist copolymer in accordance with claim 43, wherein said process which comprises the following steps (i) to (vi):

(i) step of putting 91 g of a 2-hydroxyethyl 5-norbornene-
10 2-carboxylate, 97 g of a t-butyl 5-norbornene-2-carboxylate and 98 g of maleic anhydride into a reactor;

(ii) step of purging with a nitrogen atmosphere the reaction product of the step (i);

(iii) step of reacting for the reaction product of the step
15 (ii) for 6 hours at 65 to 120 °C under the pressure of 50 to 200 atm;

(iv) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iii);

(v) step of precipitating a residue of the solvent in a
20 ethyl ether; and

(vi) step of filtering and drying the precipitate of the step (v) to produce a photoresist copolymer.

45. A process for preparing a photoresist copolymer which
25 comprises the following steps (i) to (vii):

(i) step of putting a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and a vinylene carbonate into a reactor;

(ii) step of adding a tetrahydrofuran solvent into the
30 reaction product of the step (i);

(iii) step of adding an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step
35 (iii) for 5 to 8 hours at a temperature of 50 to 80 °C;

(v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

5 (vii) step of filtering and drying the precipitate of the step (vi) to produce a photoresist copolymer.

46. A process for preparing a photoresist copolymer in accordance with claim 45, wherein said process which comprises
10 the following steps (i) to (vii):

(i) step of putting 98 g of a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and 86 g of a vinylene carbonate into a reactor;

(ii) step of adding 2 L of a tetrahydrofuran solvent into
15 the reaction product of the step (i);

(iii) step of adding 1.5 g of an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step
20 (iii) for 6 hours at 65 °C;

(v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

25 (vii) step of filtering and drying the precipitate of the step (vi) to produce a photoresist copolymer.

47. A process for preparing a photoresist copolymer which comprises the following steps (i) to (vii):

30 (i) step of putting a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and a maleic anhydride into a reactor;

(ii) step of adding a tetrahydrofuran solvent into the reaction product of the step (i);

35 (iii) step of adding an azobisisobutyronitrile (AIBN) into

the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step (iii) for 5 to 8 hours at a temperature of 50 to 80 °C;

5 (v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

(vii) step of filtering and drying the precipitate of the
10 step (vi) to produce a photoresist copolymer.

48. A process for preparing a photoresist copolymer in accordance with claim 47, wherein said process which comprises the following steps (i) to (vii):

15 (i) step of putting 98 g of a bicyclo[2,2,2] oct-5-ene-2-hydroxyethyl, 104 g of a bicyclo[2,2,2] oct-5-ene-t-butylacrylate and 98 g of a maleic anhydride into a reactor;

(ii) step of adding 2 L of a tetrahydrofuran solvent into the reaction product of the step (i);

20 (iii) step of adding 1.5 g of an azobisisobutyronitrile (AIBN) into the reaction product of the step (ii) and then purging with nitrogen atmosphere the reactor;

(iv) step of reacting for the reaction product of the step (iii) for 6 hours at 65 °C;

25 (v) step of removing a part of the solvent by a rotary evaporator after the completion of the step (iv);

(vi) step of precipitating a residue of the solvent in a ethyl ether; and

(vii) step of filtering and drying the precipitate of the
30 step (vi) to produce a photoresist copolymer.

49. A process for preparing a photoresist copolymer which comprises the following steps (i) to (iv):

(i) step of dissolving 1 mole of maleic anhydride of the
35 following formula IX, 0.05 to 0.8 moles of a 2-hydroxyethyl 5-

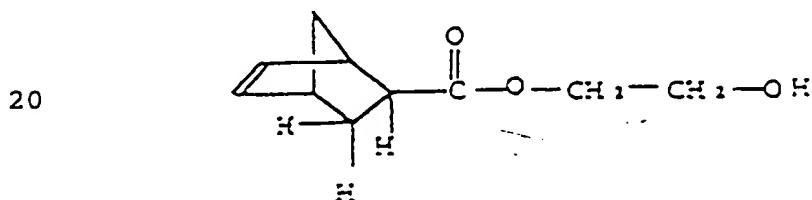
norbornene-2-carboxylate, 0.5 to 0.95 moles of t-butyl 5-norbornene-2-carboxylate and 0.01 to 0.2 moles of 5-norbornene-2-carboxylic acid in tetrahydrofuran or toluene solvent;

(ii) step of putting 0.5 to 1.0 g of an azobisisobutyronitrile (AIBN) initiator in the reaction product of the step (i);

(iii) step of reacting the reaction product of the step (ii) for 4 to 24 hours at 65 to 70 °C under a nitrogen or argon atmosphere; and

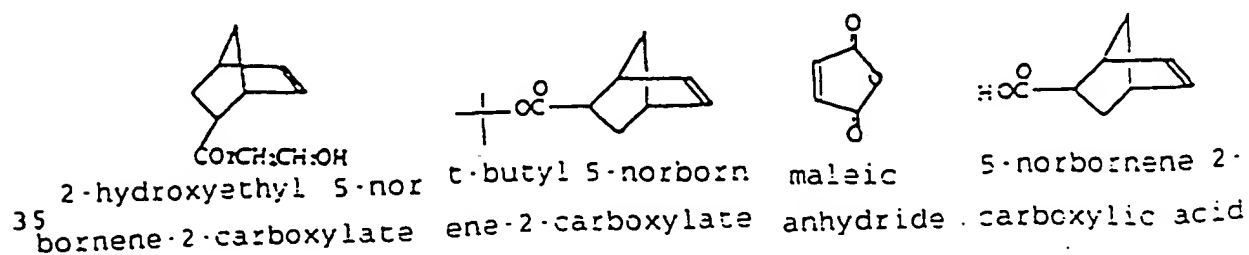
(iv) step of precipitating and drying the reaction product of the step (iii) to produce poly (2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene-2-carboxylate / maleic anhydride) photoresist copolymer.

50. A photoresist copolymer which comprises a monomer of 2-hydroxyethyl 5-norbornene-2-carboxylate of the following formula VIII:

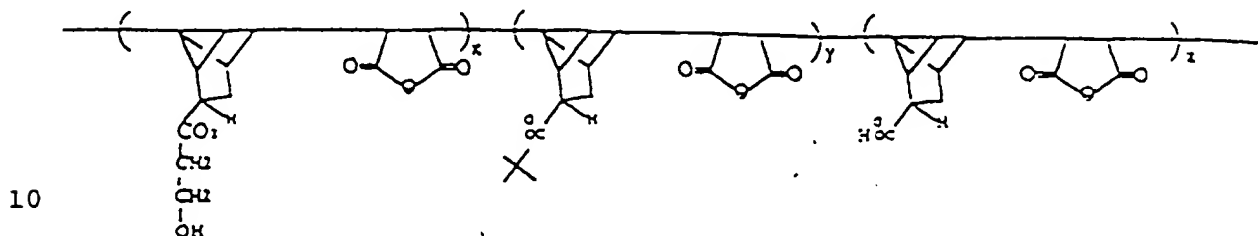


51. A photoresist copolymer in accordance with claim 50, wherein said monomer is synthesized from cyclopentadiene and 2-hydroxyethyl acrylate.

52. A photoresist copolymer in accordance with claim 50, wherein said monomer is prepared by polymerizing said repeating unit with the monomer of the following formula IX:



53. A photoresist copolymer in accordance with claim 50, wherein said resin comprising poly(2-hydroxyethyl 5-norbornene-2-carboxylate / t-butyl 5-norbornene-2-carboxylate / 5-norbornene 2-carboxylic acid / maleic anhydride) of the following formula X:



54. A method of fabricating an integrated circuit device, said method comprising steps of:

- 15 providing a substrate;
 applying a film of resist comprising a photoresist copolymer being polymerized from one or more compounds selected from one or more bicycloalkenes of the following formula II, maleic anhydride of the following formula III or vinylene carbonate the following formula IV;
- 20 exposing a portion of the film of resist using electromagnetic radiation; and
 developing said film of resist to form an exposed portion of said substrate corresponding to said portion of said exposed film and performing a process of semiconductor manufacturing on said exposed portion of said substrate.

[FORMULA II]

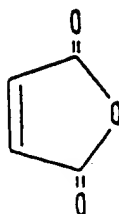


35 wherein R represents hydrogen or a straight or branched alkyl

containing 1-10 substituted or non-substituted carbon atoms; and
n is 1 or 2,

[FORMULA III]

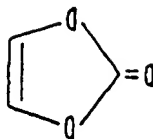
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[FORMULA IV]

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20 55. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-
25 carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

56. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said R is selected from the
30 group including hydrogen, 2-hydroxyethyl, and t-butyl.

57. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said copolymer ranges, in molecular weight, from about 3,000 to 100,000.

35

58. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said one or more compounds selected from the group including one or more bicycloalkenes of the formula II, a maleic anhydride of the formula III or a
 5 vinylene carbonate of the formula IV are copolymerized using radical polymerization initiators.

59. A method of fabricating an integrated circuit device in accordance with claim 54, wherein said photoresist copolymer is
 10 prepared by copolymerizing vinylene carbonate and one or more bicycloalkenes wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1 using radical polymerization initiators.

60. A method of fabricating an integrated circuit device in accordance with any one of claim 58 and 59, wherein said radical polymerization initiators are selected from the group including benzoylperoxide, 2, 2'-azobisisobutyronitrile (AIBN), acetylperoxide, lauryl peroxide and t-butylperacetate.

20 61. A partially completely semiconductor device, said device comprising:

a substrate; and

a film of resist comprising a photoresist copolymer being polymerized from one or more compounds selected from one or more
 25 bicycloalkenes of the following formula II, maleic anhydride of the following formula III or vinylene carbonate the following formula IV overlying said substrate.

[FORMULA II]

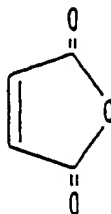


35 wherein R represents hydrogen or a straight or branched alkyl

containing 1-10 substituted or non-substituted carbon atoms; and
n is 1 or 2,

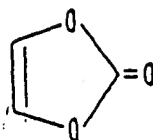
[FORMULA III]

5



[FORMULA IV]

10



15 62. A partially completely semiconductor device in accordance
with claim 61, wherein said bicycloalkenes are selected from the
group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-
butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic
acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-
20 butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and
bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.

63. A partially completely semiconductor device in accordance
with claim 61, wherein said 'R is selected from the group
25 including hydrogen, 2-hydroxyethyl, and t-butyl.

64. A partially completely semiconductor device in accordance
with claim 61, wherein said copolymer ranges, in molecular
weight, from about 3,000 to 100,000.

30

65. A partially completely semiconductor device in accordance
with claim 61, wherein said photoresist copolymer is prepared by
copolymerizing vinylene carbonate and one or more bicycloalkenes
wherein R is hydrogen, 2-hydroxyethyl or t-butyl and n is 1.

35

66. A partially completely semiconductor device in accordance with claim 65, wherein said bicycloalkenes are selected from the group including 2-hydroxyethyl 5-norbornene-2-carboxylate, t-butyl 5-norbornene-2-carboxylate, 5-norbornene 2-carboxylic acid, 2-hydroxyethyl bicyclo [2,2,2]oct-5-ene-2-carboxylate, t-butyl bicyclo[2,2,2]oct-5-ene-2-carboxylate and bicyclo[2,2,2]oct-5-ene-2-carboxylic acid.



The
Patent
Office

SS

Application No: GB 9727474.0
Claims searched: 1-34, 41-66

Examiner: Alan Kerry
Date of search: 18 March 1998

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.P): C3P PCA

Int CI (Ed.6): C08F 32/08, 232/08; C08G 61/08; G03F 7/038, 7/039

Other: Online databases: WPI, CLAIMS, CAS ONLINE

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X, P	WO 97/33198 A1 (GOODRICH) - see Examples 1-27	1, 7, 17, 23, 54 at least
X	WO 96/37526 A1 (GOODRICH) - see Claim 1 and Examples 14, 15, 30 & 31	1, 7 at least
X, P	CA Abstract 127:227308 & Proc. SPIE-Int. Soc. Opt. Eng. (1997) 3049 (Advances in Resist Technology and Processing XIV) 92-103	1, 7, 17, 23, 54 at least
X, P	CA Abstract 127:227269 & J. Photopolym. Sci. Technol. (1997) 10(4) 529-534	1, 7, 17, 23, 54 at least
X	CA Abstract 66:18889 & Magy. Kem. Foly. (1966) 72(11) 491-3	1, 7 at least

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| X | Document indicating lack of novelty or inventive step | A | Document indicating technological background and/or state of the art. |
| Y | Document indicating lack of inventive step if combined with one or more other documents of same category. | P | Document published on or after the declared priority date but before the filing date of this invention. |
| & | Member of the same patent family | E | Patent document published on or after, but with priority date earlier than, the filing date of this application. |